Defense Threat Reduction Agency
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TECHNICAL REPORT

Study of Charge Transport in Vertically- Aligned Nitride Nanowire Based Core Shell P-I-N Junctions

July 2016

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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. **PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.**

1. REPORT DATE (DD-MM-YYYY) 00-07-2016	2. REPORT TYPE Final Report	3. DATES COVERED (From - To) 1-Nov-2013 - 30-Jun-2015

4. TITLE AND SUBTITLE	5a. CONTRACT NUMBER
Study of Charge Transport in Vertically-Aligned Nitride Nanowire Based Core Shell P-I-N Junctions	5b. GRANT NUMBER HDTRA1-14-1-0003
	5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)	5d. PROJECT NUMBER
Sergiy Krylyuk, Ratan Debnath, JongYoon Ha, Albert V. Davydov, Matthew King, and Abhishek Motayed	5e. TASK NUMBER
	5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)	8. PERFORMING ORGANIZATION REPORT NUMBER
University of Maryland, 3112 Lee Building, College Park, Maryland Northrop Grumman Electronics Systems, Baltimore, Maryland	

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR'S ACRONYM(S)
Defense Threat Reduction Agency 8725 John J. Kingman Road Fort Belvoir, VA 22060-6201	DTRA
	11. SPONSOR/MONITOR'S REPORT NUMBER(S) DTRA-TR-16-34

12. DISTRIBUTION / AVAILABILITY STATEMENT

Distribution Statement A. Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

We investigated charge transport in large-area arrays of vertically-aligned, gallium nitride (GaN) based core-shell p-i-n (PIN) diodes. The proposed design can potentially produce photodetectors with efficiencies comparable to or better than traditional photomultiplier tubes (PMTs) with significant reduction in Size, Weight, and Power (SWAP). Our approach combines the precision and scalability of top-down processing with the enhanced material quality obtained through selective epitaxy to realize these structures. Vertically-aligned, radial core-shell architecture allows for significant defect reduction, strain engineering, polarity controlled growth, and transformative new device designs.

15. SUBJECT TERMS

Gallium Nitride, pin diodes, avalanche diode, radiation detectors

16. SECURITY CLASSIFICATION OF: UNCLASSIFIED			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON David Petersen
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified	SAR	11	19b. TELEPHONE NUMBER (include area code) 703-767-3164

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. Z39.18

UNIT CONVERSION TABLE
U.S. customary units to and from international units of measurement[*]

U.S. Customary Units	Multiply by → ← Divide by[†]		International Units
Length/Area/Volume			
inch (in)	2.54	$\times 10^{-2}$	meter (m)
foot (ft)	3.048	$\times 10^{-1}$	meter (m)
yard (yd)	9.144	$\times 10^{-1}$	meter (m)
mile (mi, international)	1.609 344	$\times 10^{3}$	meter (m)
mile (nmi, nautical, U.S.)	1.852	$\times 10^{3}$	meter (m)
barn (b)	1	$\times 10^{-28}$	square meter (m^2)
gallon (gal, U.S. liquid)	3.785 412	$\times 10^{-3}$	cubic meter (m^3)
cubic foot (ft^3)	2.831 685	$\times 10^{-2}$	cubic meter (m^3)
Mass/Density			
pound (lb)	4.535 924	$\times 10^{-1}$	kilogram (kg)
unified atomic mass unit (amu)	1.660 539	$\times 10^{-27}$	kilogram (kg)
pound-mass per cubic foot (lb ft^{-3})	1.601 846	$\times 10^{1}$	kilogram per cubic meter (kg m^{-3})
pound-force (lbf avoirdupois)	4.448 222		newton (N)
Energy/Work/Power			
electron volt (eV)	1.602 177	$\times 10^{-19}$	joule (J)
erg	1	$\times 10^{-7}$	joule (J)
kiloton (kt) (TNT equivalent)	4.184	$\times 10^{12}$	joule (J)
British thermal unit (Btu) (thermochemical)	1.054 350	$\times 10^{3}$	joule (J)
foot-pound-force (ft lbf)	1.355 818		joule (J)
calorie (cal) (thermochemical)	4.184		joule (J)
Pressure			
atmosphere (atm)	1.013 250	$\times 10^{5}$	pascal (Pa)
pound force per square inch (psi)	6.984 757	$\times 10^{3}$	pascal (Pa)
Temperature			
degree Fahrenheit (^{o}F)	[T(^{o}F) − 32]/1.8		degree Celsius (^{o}C)
degree Fahrenheit (^{o}F)	[T(^{o}F) + 459.67]/1.8		kelvin (K)
Radiation			
curie (Ci) [activity of radionuclides]	3.7	$\times 10^{10}$	per second (s^{-1}) [becquerel (Bq)]
roentgen (R) [air exposure]	2.579 760	$\times 10^{-4}$	coulomb per kilogram (C kg^{-1})
rad [absorbed dose]	1	$\times 10^{-2}$	joule per kilogram (J kg^{-1}) [gray (Gy)]
rem [equivalent and effective dose]	1	$\times 10^{-2}$	joule per kilogram (J kg^{-1}) [sievert (Sv)]

[*]Specific details regarding the implementation of SI units may be viewed at http://www.bipm.org/en/si/.
[†]Multiply the U.S. customary unit by the factor to get the international unit. Divide the international unit by the factor to get the U.S. customary unit.

2015-11-16

Final Report

Study of Charge Transport in Vertically-Aligned Nitride Nanowire Based Core Shell P-I-N Junctions

Principal Investigator:
Abhishek Motayed
University of Maryland

Study of Charge Transport in Vertically-Aligned Nitride Nanowire Based Core-Shell PIN Diodes

I.   ABSTRACT.

We have studies charge transport and developed high-efficiency, solid-state photodetectors using large-area arrays of vertically-aligned, gallium nitride (GaN) based core-shell p-i-n (PIN) diodes. The proposed design can potentially produce photodetectors with efficiencies comparable to or better than traditional photomultiplier tubes (PMTs) with significant reduction in **S**ize, **W**eight, **a**nd **P**ower (SWAP). Current C-WMD operational capability is severely limited when utilizing PMTs, given their fragility and performance instabilities when exposed to external stimuli such as vibration, E- or B-fields and high photon fluxes. Nanoengineered nitride-based PIN diodes can completely circumvent these issues and bring to bear an unprecedented level of ruggedness and performance. Through this Fundamental Research program we will demonstrate a pathway to C-WMD detectors with high gain (M $\geq$ 50,000), low excess noise factor (F<5) and large areas (arrays with 1-10 mm^2 pixel size), which are insensitive to a battery of external stimuli.

The nitride material system, with tunable direct bandgaps (200 nm for AlN to ~1 μm for InN) and robust material properties, is ideally suited for the development of visible-blind UV photodetectors needed for the next-generation of scintillators in field-deployed radiation detectors. Traditional GaN based thin-film photodetectors suffer from strain, defects, and detrimental polarization effects resulting from heteroepitaxial growth of thin layers on non-native substrates. Although bottom-up growth methods (e.g. catalyst-based nanowire growth) have shown significant promise in terms of realizing defect-free structures, they face insurmountable challenges in scaling up and reproducibility necessary for large-area applications. Our approach combines the precision and scalability of top-down processing with the enhanced material quality obtained through selective epitaxy to realize these structures. Vertically-aligned, radial core-shell architecture allows for significant defect reduction, strain engineering, polarity controlled growth, and transformative new device designs - otherwise not possible in traditional thin-film structures. This project successfully combines University of Maryland team's unmatched experience in nitride device design and fabrication with Northrop Grumman's expertise in nitride materials growth and radiological/nuclear detection systems, and National Institute of Standards and Technology's exceptional nanofabrication and characterization capabilities.

II.   SCOPE.

The proposed research aims to investigate novel vertically-aligned nitride core-shell devices as highly-viable replacements for current PMT technologies, with detection efficiency, responsivity, and noise comparable to state-of-the-art PMT-based detectors. The specific objectives include: 1) design and simulation of core-shell structures for realistic estimation of performance metrics achievable from such structures and further refinement of the design, 2) development of growth expertise for control of defects, dopants, and morphology in both thin films and overgrowths with an aim to improve material quality, and 3) fabrication of device structures and their extensive characterization. The emphasis of all the objectives is to investigate the feasibility of operating these structures in the impact ionization field regimes, which would produce avalanche multiplication, hence current gains required for sensitive photodetection. The challenges of operating nitride-based photodetectors at breakdown biases are two folds: materials

and device-related. Both of which, we believe could be resolved by our innovative vertically-aligned core-shell p-i-n structures.

A. **OBJECTIVE.**

The proposed research will be focused on the demonstration of a working photodetector chip containing integrated arrays of individual core-shell PIN diodes. At the end of this program we will have demonstrated a working nanoengineered nitride-based avalanche photodiode and we will have fully characterized the device level performance of this novel structure. A natural byproduct of this development is evaluating the extent to which such photodetectors can be utilized in C-WMD applications. Significant efforts will be dedicated towards device design, materials development, development and optimization of the fabrication processes, and collection of operational parameters (dark current, quantum efficiency, responsivity, noise power, breakdown voltage) of fabricated devices. We will also consider lab-bench level integration strategies and peripheral interface electronics for future system-level integration.
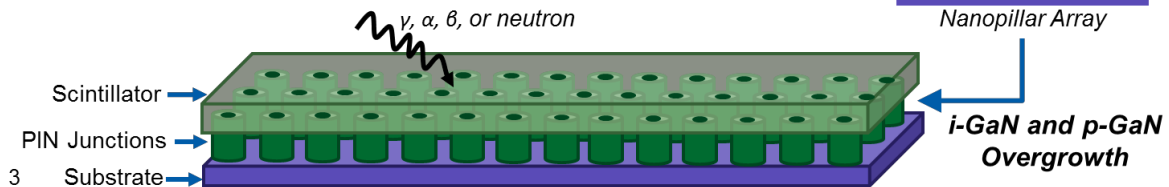
Our efforts will include:

1) Developing 2-D and 3-D advanced device modeling efforts using industry-standard, high performance device simulator from Silvaco^{TM}, allowing for designing high-efficiency devices
2) Developing a strong nitride epitaxial growth program partnering with Northrop Grumman-Electronic Systems, required for the proposed novel device design
3) Wafer-scale nano-patterning with (a) control over shape and morphology, (b) defect free smooth surface of the etched side-walls and base plane, (c) ability to tailor profiles for specific designs, and (d) large-area uniformity and scalability
4) Controlled overgrowth for device structure development with dopant control
5) Complete device fabrication with various process optimization for enhanced detector performance
6) Studying the photodetector performance and reliability (parametric variations and high electric-field induced damage) in design-variants through extensive characterization

The following sections describe the approach and results obtained.

# Approach for Efficient Solid State Photon Counting in Near-UV

- GaN (n-type) films will be etched to create "nanopillar" arrays

- The pillar arrays will then undergo two overgrowth stages: i-GaN and p-GaN, in sequence

- This structure—a radial/core-shell PIN junction—could be capable of increased efficiency photodetection
    - Active area will be directly exposed to incident photons—will not have problems with absorption outside the depletion region

- The structure will also provide insight into fundamental charge carrier generation and collection mechanisms in the nitride system
    - Impact of various classes of defects will be apparent

- *Coupled to a SrI$_2$ scintillator, this structure could be the next generation radiation detection system*

n+ GaN
Al$_x$Ga$_{(x-1)}$N
AlN
Si

AlN/AlGaN/GaN on Si

Dry Etch Process

Nanopillar Array

i-GaN and p-GaN Overgrowth

γ, α, β, or neutron

Scintillator →
PIN Junctions →
3 Substrate →

SOA: Need Vertical P-N Diode Geometry to Increase Detector Efficiency
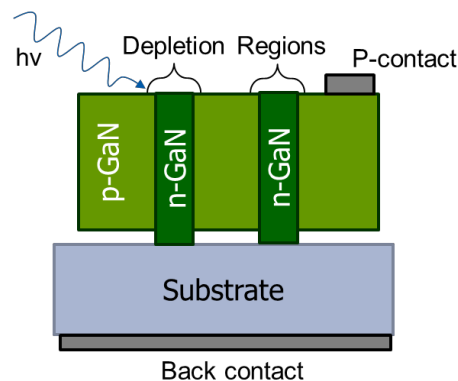

Conventional GaN PN Junction
- **Losses due to absorption in the p-layer**
- **Defect density ~ 10^{10} cm^{-3}**
- **Internal E-field due to lattice polarity—junction exists on polar [0001] plane**
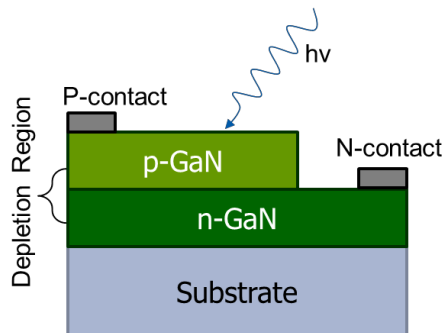
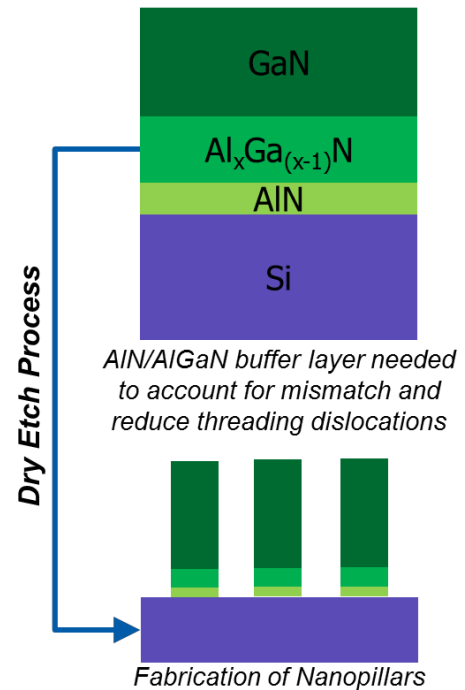**Vertical PN Junction Geometry**
- **Depletion region directly exposed to photons—no p-GaN absorption**
- **Defect density < 10^6 cm^{-3}**
- **No internal E-field—junction exists on non-polar [1$\bar{1}$00] or [11$\bar{2}$0] plane**

hv

P-contact
p-GaN
N-contact
n-GaN
Substrate
Depletion Region

Depletion Regions
hv
P-contact
p-GaN   n-GaN   n-GaN
Substrate
Back contact

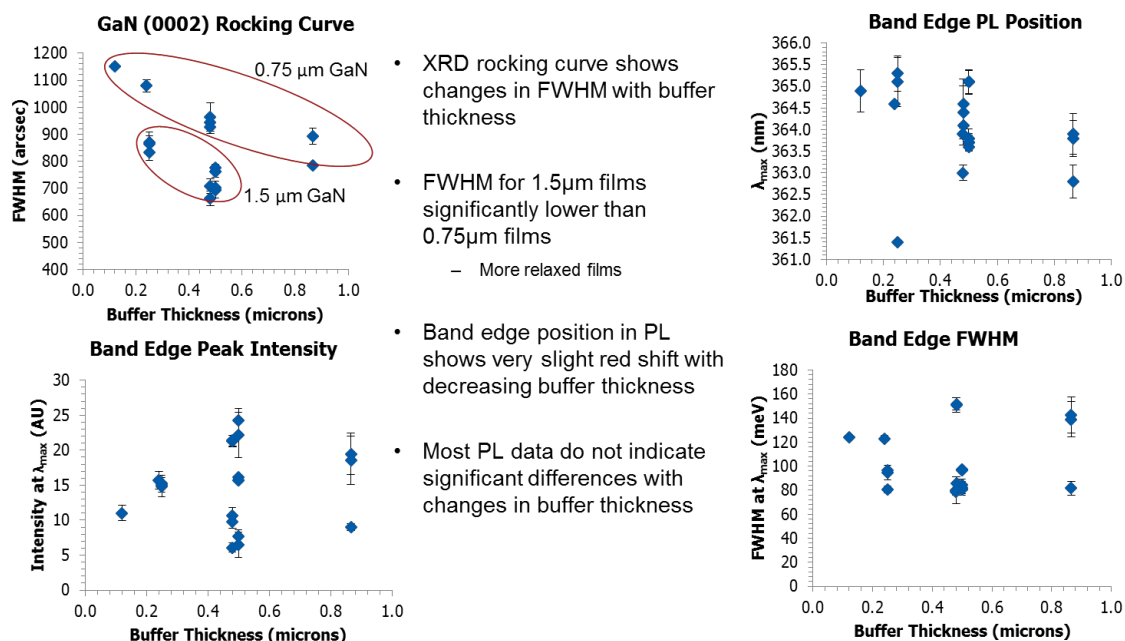**Novel Vertical Geometry Increases PN Junction Detector Efficiency**   4

Epitaxial GaN on Si Forms the Basis for Nanopillar PIN Junctions

- Goal: Grow high quality, thick (>1μm) GaN on Si
  - Requires an AlN/AlGaN buffer layer to compensate for lattice mismatch between Si and GaN
  - Buffer layer will negatively impact device performance by changing the amount of active area available in the PIN junction
  - Need to balance material quality (requires large buffer) and device performance (requires smaller buffer)

- Approach: Incrementally reduce buffer thickness and measure effect on quality
  - XRD (GaN rocking curve)
  - PL (Band edge intensity, FWHM, defect emission)
  - Electrical (mobility, carrier density, sheet resistance)

| GaN |
| Al$_x$Ga$_{(x-1)}$N |
| AlN |
| Si |

Dry Etch Process

AlN/AlGaN buffer layer needed to account for mismatch and reduce threading dislocations

Fabrication of Nanopillars

Ultimate Goal: High Quality GaN Nanopillars

Need Thin Buffer Between Si and GaN Template for Electrical Conductivity

GaN (0002) Rocking Curve

0.75 μm GaN

1.5 μm GaN

FWHM (arcsec) vs Buffer Thickness (microns)

- XRD rocking curve shows changes in FWHM with buffer thickness

- FWHM for 1.5μm films significantly lower than 0.75μm films
  - More relaxed films

- Band edge position in PL shows very slight red shift with decreasing buffer thickness

- Most PL data do not indicate significant differences with changes in buffer thickness

Band Edge PL Position

λ_{max} (nm) vs Buffer Thickness (microns)

Band Edge Peak Intensity

Intensity at λ_{max} (AU) vs Buffer Thickness (microns)

Band Edge FWHM

FWHM at λ_{max} (meV) vs Buffer Thickness (microns)

High Quality GaN on Si Optimized for Nanopillar Fabrication

Mask Design Enables Control of GaN Pillar Morphology and NanoAPD Array Properties

- 1st Mask is an array of shapes (7 total)
  - Various diameters (10-0.25µm) and densities (20x20µm to 0.5x0.5µm)
  - Will determine the effect of pillar shape on optical/electrical properties, e.g. charge carrier mobility and collection
  - Varying array densities will allow for optimization of overgrowth process

- Metal chosen as hard mask for RIE processing

- DUV stepper + liftoff to achieve shape arrays
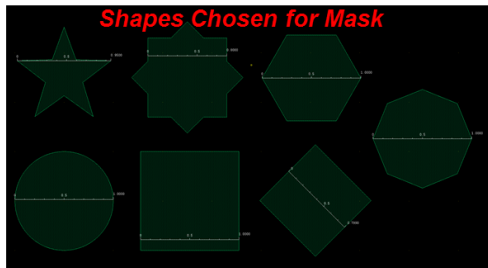
Mask Layout for Pillar Arrays
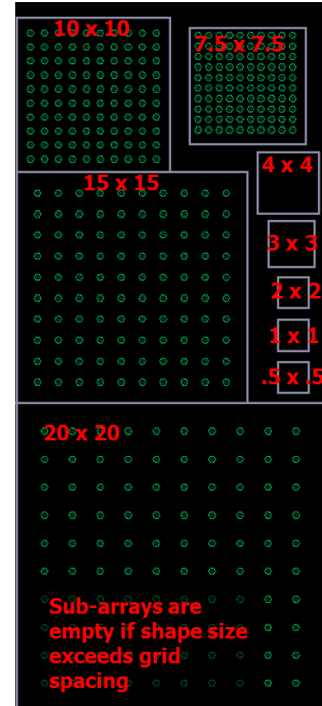
8

Photolithography Optimization Enables Sub-Micron Array Fidelity

- Some features not present in most cases
  - Features <250nm, with the exception of squares

- Small features found in other locations on the substrate
  - Poor adhesion

- Approach to solve problem with small features:
  - Add Ti adhesion layer
  - Optimize exposure, development and liftoff
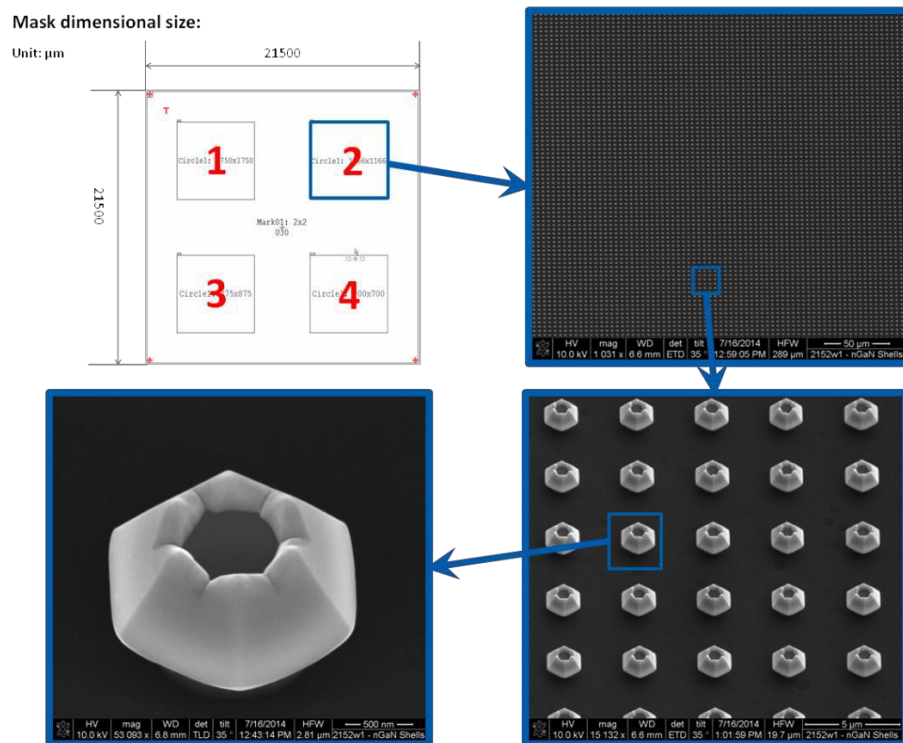

*Rounding apparent for smaller features*

Decreasing Size

9

6

Second Mask Design for Very Large NanoAPD Arrays

10

Dry Etching Process Development Needed for Fabrication of GaN Nanopillars
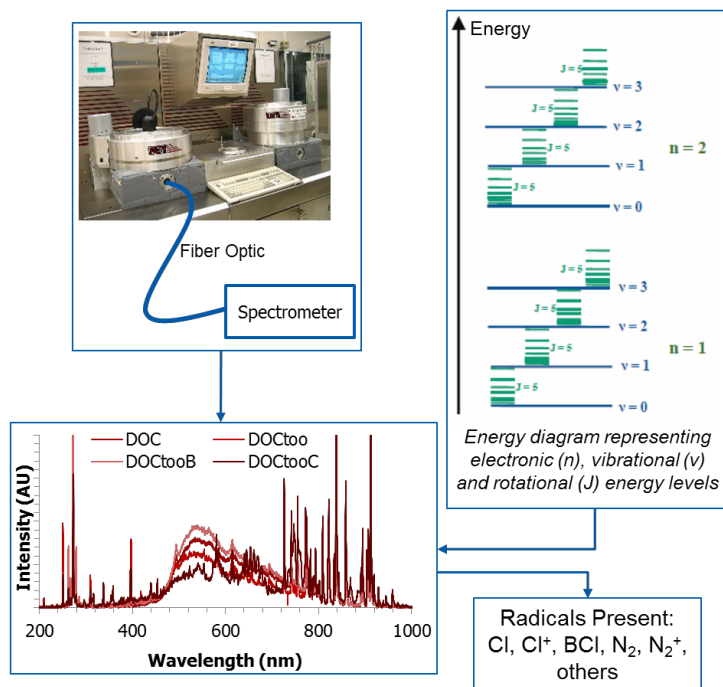
- Reactive Ion Etching
  - Gas: combination of Cl_2, BCl_3, N_2
  - Pressure: 2-10mTorr
  - ICP Power: 800W
  - RIE Power: 20-90

- Initial Etch Recipe
  - Low power, high pressure, Cl_2/BCl_3
  - **Poor sidewall angle: 65-70°**
  - Low etch rate and low Al/Ga selectivity

- Modified Recipe
  - High power, low pressure, *incorporation of N_2 in process gas*
  - **Good sidewall angle: >80°**
  - Higher etch rate, better Al/Ga selectivity
  - Roughness diminished somewhat
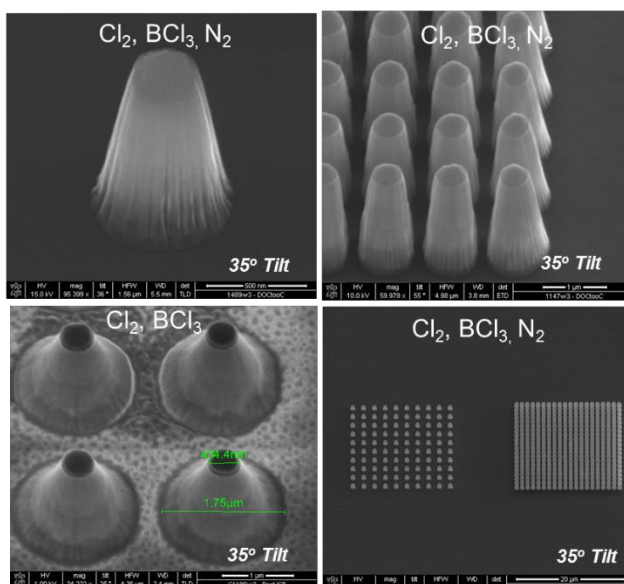
High Power + Incorporation of N_2 Drastically Decreases Sidewall Angle
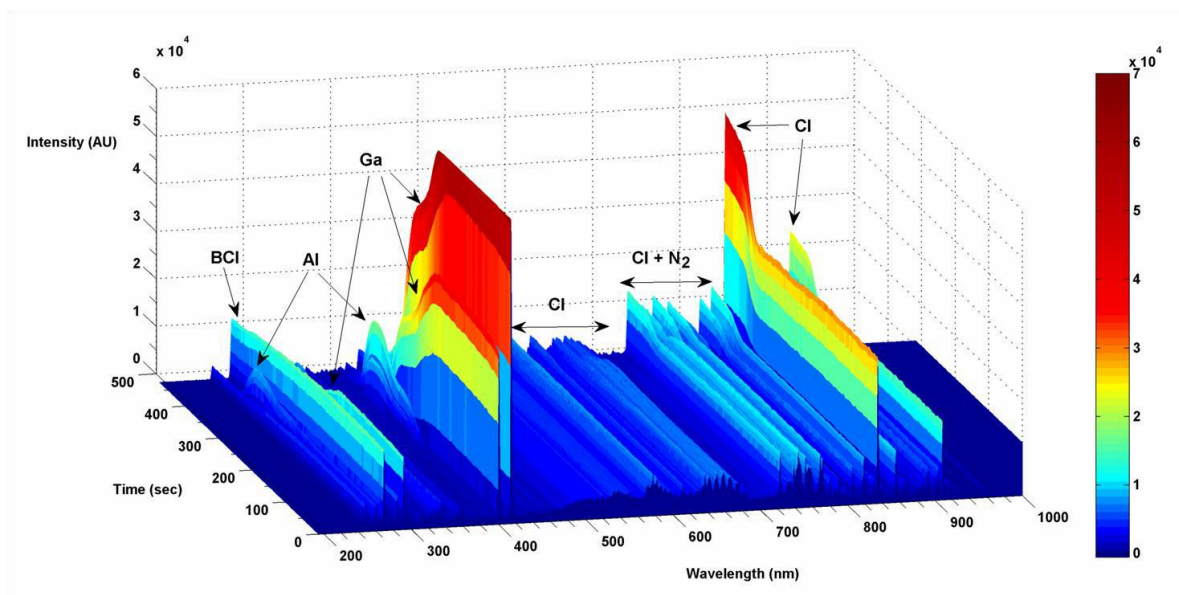
7

Optical Emission Spectroscopy (OES): Analysis of Plasma Chemistry for End Point Detection

- Excitation of gaseous species in the plasma facilitates light emission

- Peaks are characteristic of specific atoms and molecules

- Analysis can indicate which species are present and active

- Great for end point detection

Fiber Optic

Spectrometer

Energy diagram representing electronic (n), vibrational (v) and rotational (J) energy levels

Radicals Present: Cl, Cl⁺, BCl, N_2, N_2^+, others

12

Northrop Grumman Private Proprietary Level I

OES Analysis as a Function of Time

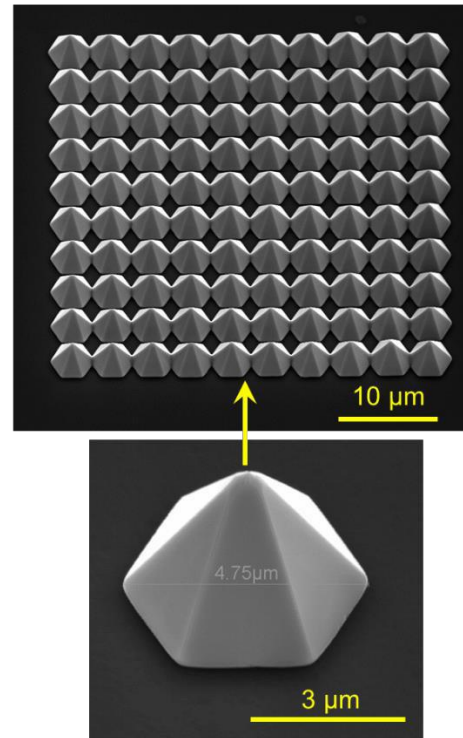OES Provides Key Insights into GaN Etching Process vs. Time

13

8

MOCVD-Based Shell Growth Shows Promise for n-type and i-type GaN

<u>Benefits of MOCVD Growth</u>

- Atomically smooth surfaces

- Reduced growth rate engenders superior junction thickness control

- Reduced impurity incorporation

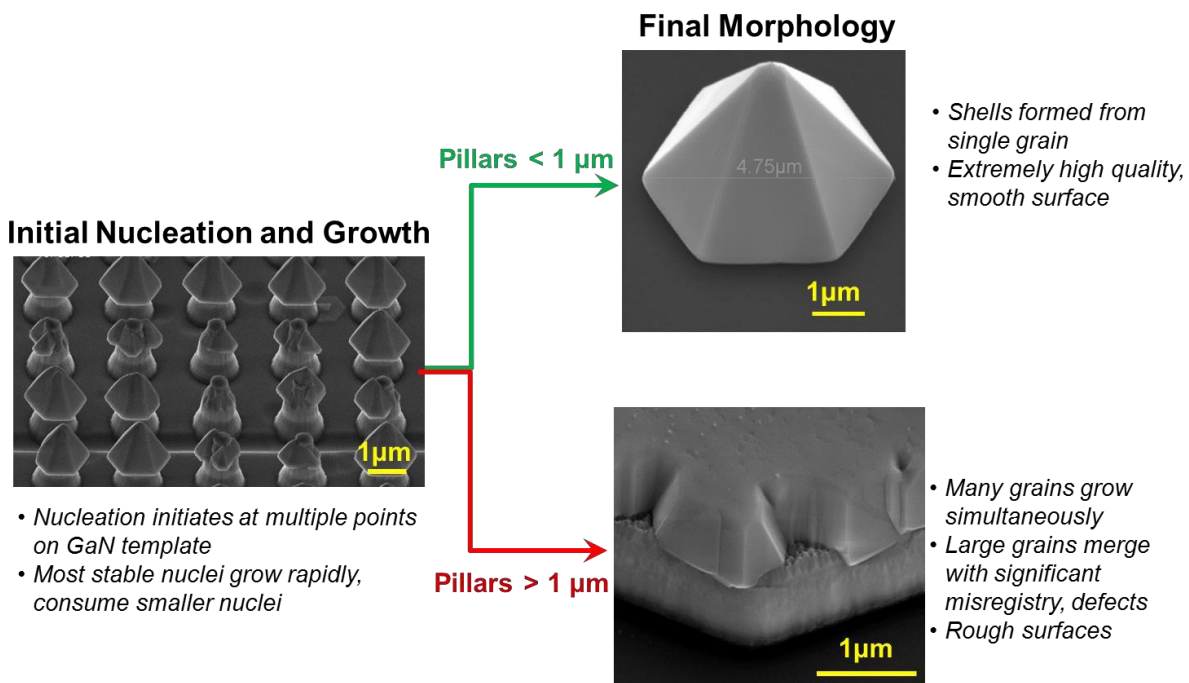- Shell sidewall polarity can be controlled using growth parameters

<u>Future Development</u>

- Develop dopant incorporation control for n-type and insulating GaN

- Calibrate growth parameters for shell thickness and sidewall polarity

16

10 µm

4.75µm

3 µm

Nanoscale GaN Templates Enable Exclusive Crystal Quality

Final Morphology

4.75µm

1µm

Pillars < 1 µm

- *Shells formed from single grain*
- *Extremely high quality, smooth surface*

Initial Nucleation and Growth

1µm

- *Nucleation initiates at multiple points on GaN template*
- *Most stable nuclei grow rapidly, consume smaller nuclei*

Pillars > 1 µm

1µm

- *Many grains grow simultaneously*
- *Large grains merge with significant misregistry, defects*
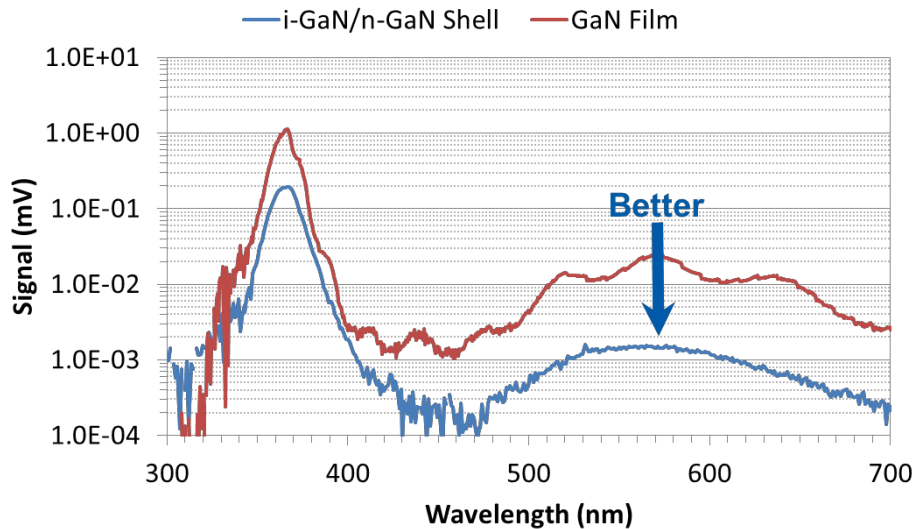- *Rough surfaces*

17 Conventional Feature Sizes Incapable of Producing Necessary Quality

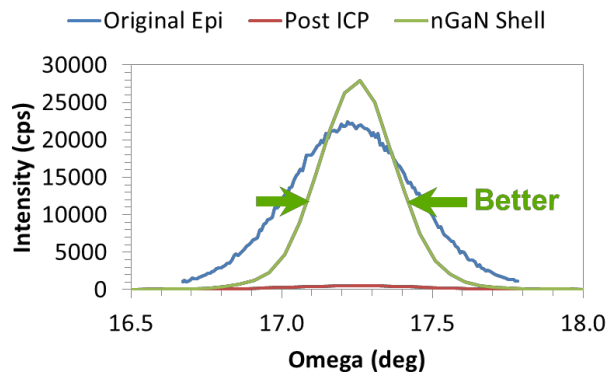## Photoluminescence Studies Show Superior Quality of MOCVD GaN Shells

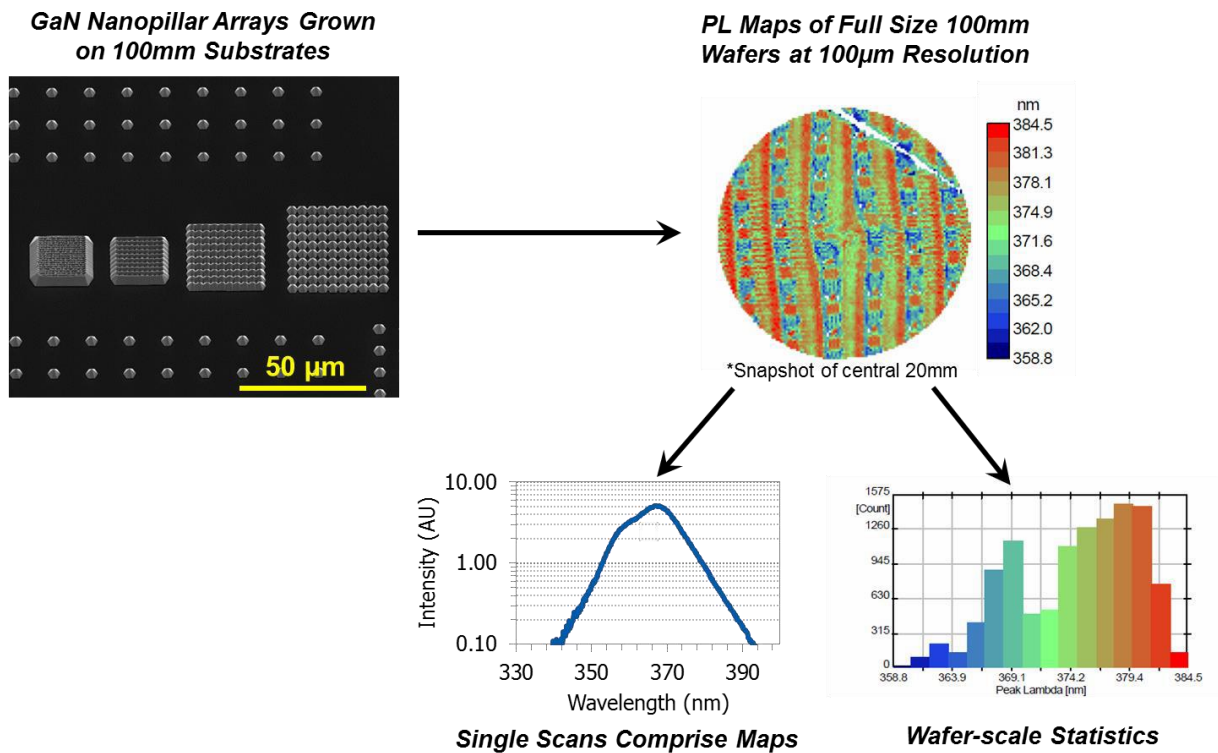| Peak Ratios: Band Edge/Yellow Defect Emission	
As Grown Epi	44.7
i-GaN/n-GaN Shell Growth	129.8

19

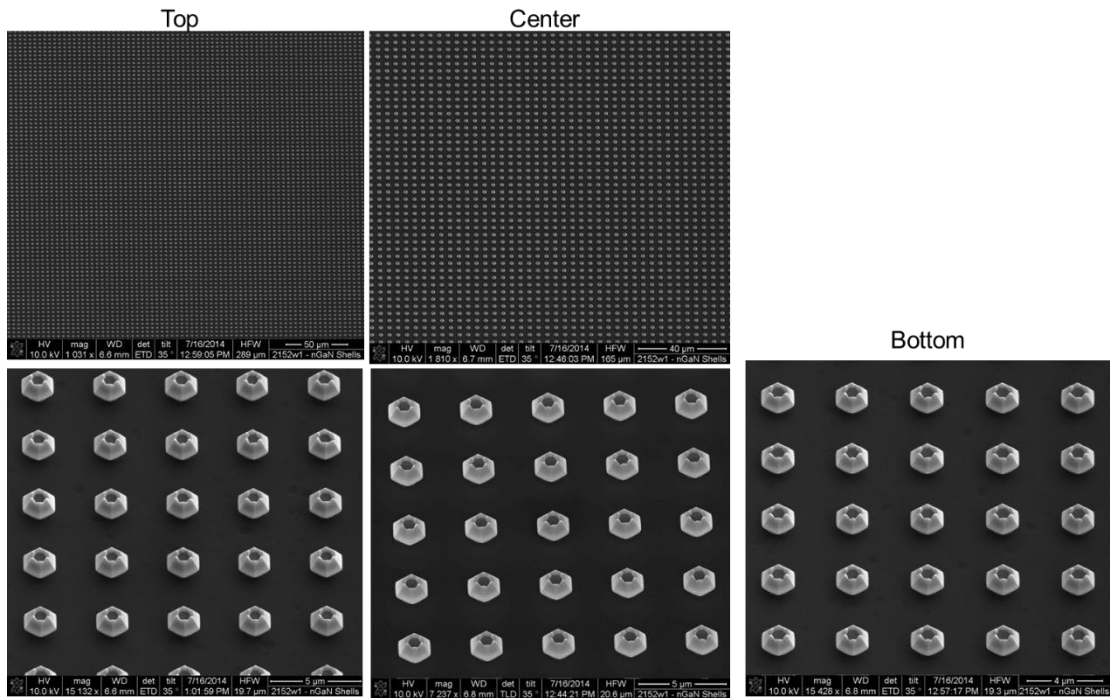## X-Ray Diffraction Also Shows Significant Improvement Over Original Epi Quality

Sample	Peak Intensity (cps)	FWHM (°)
Original Epi	22225	0.488
Etched Pillars	547	0.498
n-GaN Shell	**27897**	**0.284**

20

Large Area, High Resolution PL Maps Allow In-Depth Growth Uniformity Analysis

GaN Nanopillar Arrays Grown on 100mm Substrates

PL Maps of Full Size 100mm Wafers at 100μm Resolution

*Snapshot of central 20mm

Single Scans Comprise Maps

Wafer-scale Statistics

21

MOCVD GaN Shell Growth Enables Controlled Morphology Over Large Area

Program Summary

- NanoAPD structure represents a viable solution for current RN detection needs

- Novel GaN Core-Shell diode approach capable of improving collection efficiency by orders of magnitude

- NGES GaN epitaxial design and growth enabled significant improvement in material quality

- Large area GaN shell growth demonstrated via MOCVD

- Further improvements in quality and uniformity will enable unprecedented detector performance

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